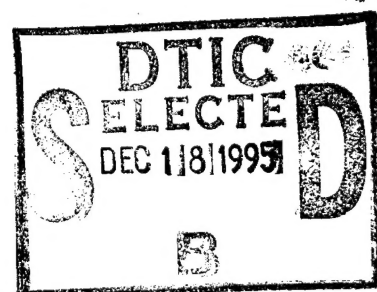


FINAL TECHNICAL REPORT  
Contract N00014-92-C-0172  
September 1995

**Ion Implantation Processes for  
Heteroepitaxial Nucleation of Diamond**

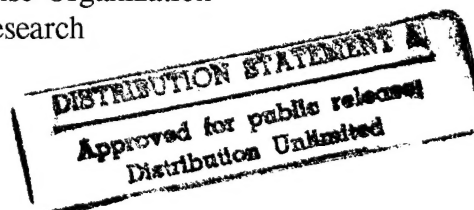
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Bedford, MA 01730

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## Ion Implantation Processes for Heteroepitaxial Nucleation of Diamond

EPION CORPORATION  
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Period Covered: 28 July 1992 - 30 April 1995

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## I. INTRODUCTION

This is the Final Technical Report under SBIR Phase II Contract N00014-C-92-0148 entitled "Single Crystal Diamond Thin Films". The report summarizes program efforts between 28 July 1992 and 28 April 1995. Investigations were conducted during two incremental 1-year periods separated by an interval of 9 months.

The objective of this program has been to identify some method to promote heteroepitaxial nucleation of diamond on a foreign substrate based upon variations of the implantation-outdiffusion concept for heteroepitaxial formation of diamond originally suggested by Prins and Gaigher in September 1990<sup>1</sup>. Prins and Gaigher proposed that if carbon is introduced by ion implantation at high temperature into a suitable substrate, such as copper, with a lattice structure similar to that of diamond and in which carbon is unreactive and not soluble, the implanted carbon atoms should be able to migrate to the surface where they will bond with other carbon atoms. If the carbon layer can be induced to form using the lattice structure of the host substrate as a template, the resulting layer might be able to serve as a heteroepitaxial nucleation interface for subsequent diamond deposition.

This Phase II program followed upon a 1991 Phase I investigation which had been directed toward utilizing the implantation-outdiffusion concept in conjunction with single crystal copper films which can be formed on single crystal silicon wafer substrates by means of an ultra-high vacuum ion-assisted deposition process<sup>2</sup>. Under the Phase I program, heteroepitaxial copper films intended to serve as starting materials for heteroepitaxial diamond growth were produced on silicon. It is reasonable to anticipate that heteroepitaxial films of other metals can be produced on silicon by similar methods. The intent of the Phase II investigation has been to determine whether some implantation-outdiffusion process variation can be established to be usable in conjunction with such films to produce starting materials for growth of large sheets of single crystal diamond.

Ion implantation investigations and CVD diamond growth studies under this program have been performed at Epion. Supporting investigations to examine the effects of high temperature conditions upon copper surfaces during carbon ion implantation have been conducted by Drs. W. K. Chu and Z. H. Zhang of the Texas Center for Superconductivity at the University of Houston. Dr. P. H. Fang of F. S. Lab in Belmont, Massachusetts has participated in the planning and conduct of high temperature ion implantation and CVD diamond growth studies performed on surfaces of various metals.

A method to employ implantation-outdiffusion for heteroepitaxial diamond growth has not been found. Graphite, not diamond, has been found to form under all implantation-outdiffusion conditions which were investigated. In addition to the problems which apparently exist with thermodynamic fundamentals, it has become recognized

that implantation-outdiffusion approaches to nucleation of diamond place difficult or impossible requirements upon the properties which must be exhibited by a host substrate. No material has been identified which is able to satisfy all of the imposed constraints. In spite of many efforts to modify the approach so as to alleviate some of the requirements, there has been no experimental evidence that carbon introduced by ion implantation into the surface of any available material can be induced to nucleate upon that surface as diamond rather than as graphite.

High temperature implantation techniques investigated under the program have been found to offer promise for orientated diamond growth, but by reactive formation of intermediary layers rather than by implantation-outdiffusion. Ion implanted carbon can react at high temperatures with some substrates to form heteroepitaxial carbide layers which might be able to serve to support heteroepitaxial diamond growth. This possibility has been observed in silicon where carbon implanted at high temperatures reacts to form a crystalline silicon carbide layer.

## II. PROGRAM OVERVIEW

The implantation-outdiffusion approach to heteroepitaxial formation of diamond which was suggested by Prins and Gaigher was based upon implantation of carbon ions into copper at high temperature<sup>1</sup>. Cu has a lattice constant similar to that of diamond and does not form a carbide. Even though carbon is almost insoluble in copper, distributions of carbon atoms can be introduced into the vicinity of a copper surface by means of ion implantation. At sufficiently high temperature, implanted C atoms should be free to diffuse to the copper surface where they are expected to combine under the influence of short range forces of the Cu lattice. The cubic crystal structure of copper with 3.6151Å lattice parameter is sufficiently similar to that of diamond with 3.5667Å lattice parameter that it might serve as a template to promote bonding of the carbon into diamond registered with the lattice of the copper host.

A number of subsequently reported C<sup>+</sup> into Cu investigations produced only a few encouraging observations<sup>3,4</sup> among mainly negative results<sup>5,6,7,8</sup>. In most cases, carbon layers on copper as a result of C<sup>+</sup> implantation at high temperatures were found to be crystalline graphite with the graphite c-axis oriented to be normal to the copper surface<sup>5,6</sup>.

At the outset of the present investigation, it was assumed that if the implantation-outdiffusion concept for heteroepitaxial nucleation of diamond was to succeed, the ion implantation processes would have to be conducted under conditions not usually available with conventional ion implantation equipment. For this purpose, Epion dedicated a Varian Model DF4 medium current 200 keV implanter to this project. The implanter was modified under the

program to allow substrates which were to be implanted to be maintained at temperatures up to 1000°C, to allow background atomic hydrogen bombardment of substrates during implantation, and to allow in-situ filament-assisted CVD diamond growth to be conducted within the implanter process chamber following completion of the ion implantation processes.

Copper was investigated extensively as a substrate material during the first year of this program. Among candidate metals, copper has been considered by most investigators to have the most favorable combination of properties for the implantation-outdiffusion approach to heteroepitaxial nucleation of diamond. These properties include a fairly good lattice match to that of diamond, very low carbon solubility even at high temperatures, and absence of chemical interactions with carbon. During the studies conducted under this program, it became evident that evaporation of the host substrate during implantation-outdiffusion processing is a critical problem. Unfortunately, copper exhibits vapor pressure which is much too high at the required temperatures. This was found to be a fatal deficiency which effectively eliminates copper as a candidate.

During this program, progress toward heteroepitaxial nucleation was made by other investigators who were able to produce oriented diamond films on nickel substrates using filament-assisted CVD by means of a pre-growth nucleation process which employed diamond seeding in conjunction with high temperature annealing performed in a hydrogen atmosphere<sup>9,10</sup>. It was proposed that the nucleation action involved physical reorientation of partially dissolved diamond seeds floating on a shallow molten surface comprised of nickel, dissolved hydrogen and carbon from the seeds themselves. Temperature/time parameters for the high temperature annealing operations were critical. Other investigators had reported that formation of nickel hydride on a nickel surface during CVD diamond growth can result in suppression of graphite formation in favor of diamond growth<sup>11</sup>. It was recognized that implantation-outdiffusion techniques might be used in conjunction with molten surface hydride layer nucleation approaches to allow other materials to be considered as potentially suitable substrates for heteroepitaxial nucleation of diamond. To this purpose, the investigations under this program were expanded to include other candidate substrates. Materials in addition to copper which were experimentally evaluated included the following:

- nickel
- niobium
- palladium
- cobalt
- zirconium
- silicon
- germanium.

### III PROGRAM INVESTIGATIONS

#### III.1 Ion Implantation Apparatus and Technique Development

An ion implantation system belonging to Epion Corporation was adapted to perform the processing required for this program. Modifications made to the 200 kV medium current Varian Model DF4 implantation system included replacement of the existing wafer handling apparatus by a separate process chamber with a vacuum entry lock and addition of a high temperature tube furnace and hot filament CVD diamond growth components into the process chamber. These modifications provided the following capabilities:

- substrate temperatures to above 1000°C
- background atomic hydrogen during implantation
- in-situ diamond growth using filament-assisted CVD.

Figure 1 is a schematic diagram of the high temperature process zone of the modified implantation apparatus. Figures 2 and 3 show the process chamber and the high temperature furnace. Substrates to be implanted are passed through a vacuum lock into the center of the tube furnace. A tungsten dissociation filament and a nozzle for introduction of gases are located in close proximity to the substrate surface.  $H_2$  background gas at low pressure can be introduced during ion implantation. Following implantation, the chamber can be isolated and backfilled with  $H_2$  and  $CH_4$  gases for filament-assisted CVD diamond growth.

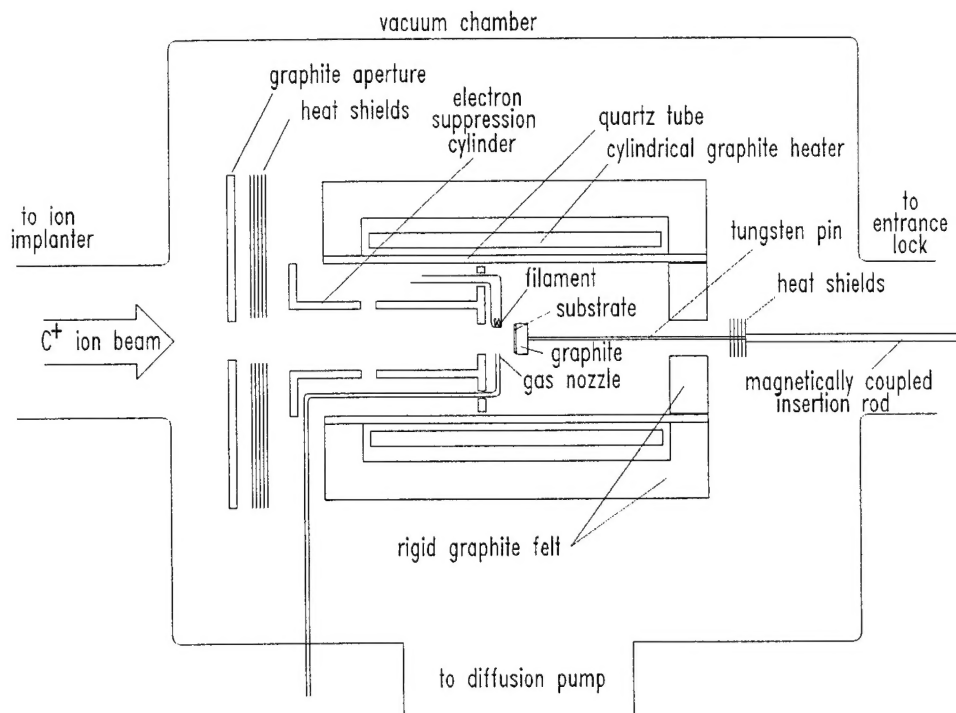


Figure 1  
Configuration of the high temperature implantation apparatus

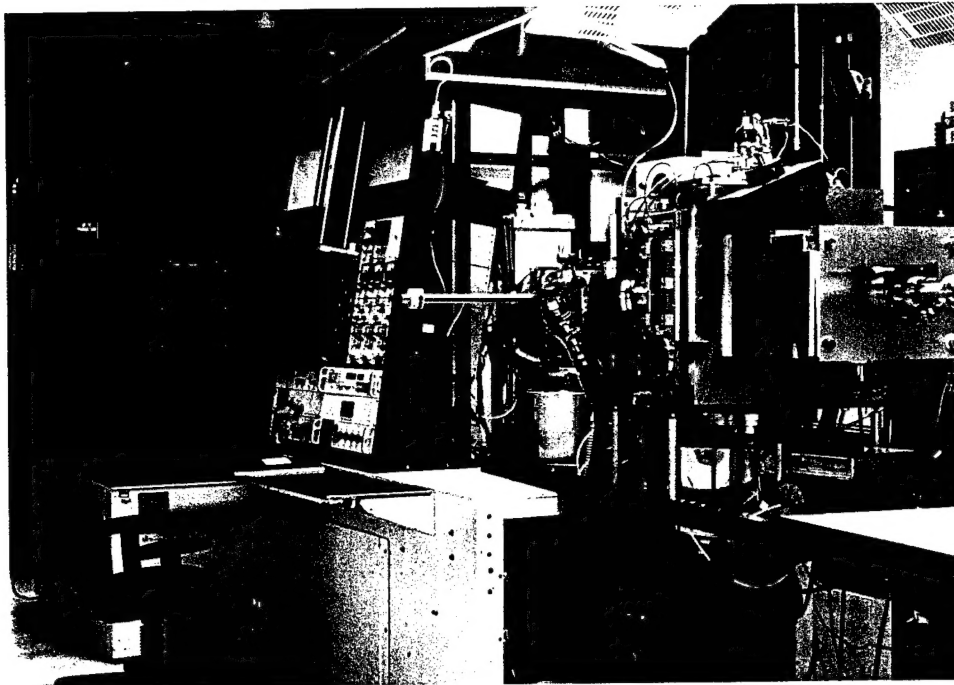


Figure 2  
Implanter modified for high temperature process studies

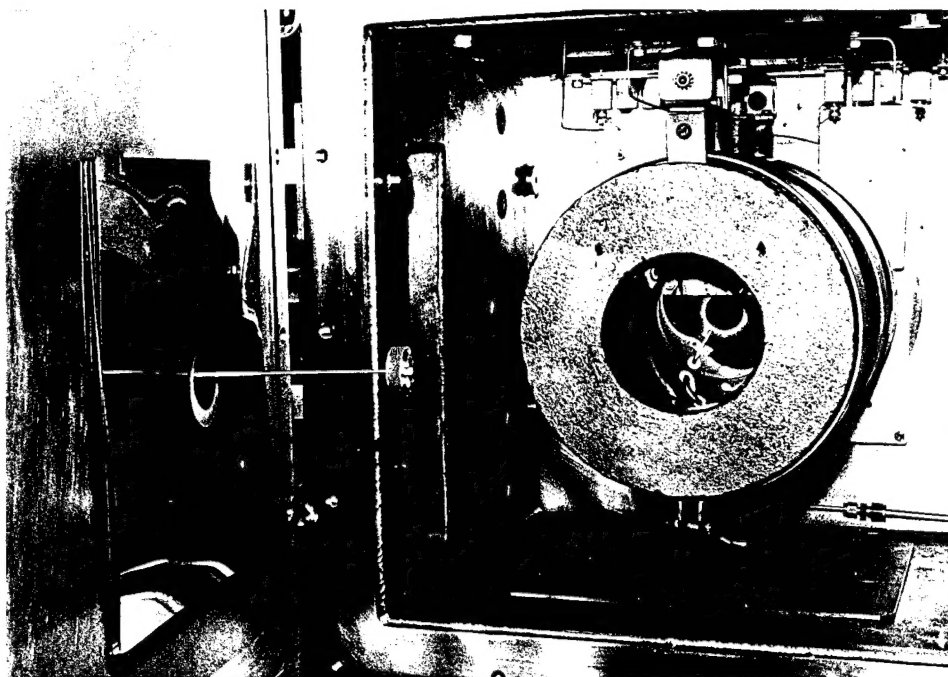


Figure 3  
Vacuum furnace for high temperature implantations



### III.2 C<sup>+</sup> into Cu Implantation-Outdiffusion Studies

The high temperature implantation apparatus developed for the program was intended to provide versatile implantation-outdiffusion process capabilities. Variables of interest were C<sup>+</sup> ion energy, dose and dose rate, substrate temperature during and after deposition, use of additional ion pre-implantation, co-implantation and post-implantation, and optional presence of background atomic hydrogen flux during implantation. Table I summarizes process conditions employed in a first series of experiments conducted using copper substrates. All these studies employed relatively high purity (99.999+%) polycrystalline Cu sheet. Polycrystalline material allowed evaluation of the possible influence of the variation of crystal orientation upon nucleation effects produced. All ion implantations were conducted into circular Cu sheet substrates 2.5 cm in diameter.

All experimental samples were examined using both optical and scanning electron microscopy. The nature of the surface effects which were investigated was such that images from either the optical microscope or the SEM were sometimes difficult to interpret. Optical images were found to be misleading when the scale of the individual surface structures which were formed was very small ( $\leq 1\mu\text{m}$ ). Electrical charging effects associated with some forms of carbon, and low signal characteristics of others, were found to result in SEM images which were difficult to interpret. Both the optical and SEM views had to be considered together to avoid misinterpretations.

It was assumed that if ion implanted C<sup>+</sup> could be induced to form diamond heteroepitaxially upon a Cu substrate, CVD could then be employed to continue growth of the heteroepitaxial diamond layer. Observations of CVD growth behavior upon experimental samples were expected to provide information regarding the character of the surface carbon layers. At least a portion of each implanted sample was subjected to a brief CVD diamond growth process so as to allow examination of the diamond nucleation effects which would take place. Some of these CVD processes were performed in-situ within the process station of the ion implantation apparatus and some were conducted in a separate filament-assisted CVD reactor at Epion following the examinations of the as-implanted samples. CVD growth behaviors on copper surfaces implanted with C<sup>+</sup> were found to depend strongly upon the C<sup>+</sup> implantation procedures and parameters. Evaluations were complicated by the fact that continuous diamond films of thicknesses greater than a fraction of a micron would always spontaneously delaminate from the copper during cooling after the deposition because of expansion coefficient mismatch and absence of strong bonding at the diamond/Cu interface. Consequently CVD layers deposited for evaluation purposes were usually kept to a few tenths of a micron in thickness.

## CARBON IMPLANTS INTO COPPER

Run #	Ion	E keV	Dose cm-2	Temp C	Filament	Gases	Time	Post Anneal
1	C	60	2.5E+17	750			6 hours	
2	C	60	1.4E+17	800			3hr/20min	
3	C	60	3.0E+16	800			6hr/34min	
4	CC	120	3.5E+16	800			4.5 hours	
5	CC	120	1.0E+16	800			3 hours	
6	CC	120	2.0E+16	700			2hr/26min	
7	CC	120	2.0E+16	800			4hr/18min	
8	CC	120	1.0E+16	900			4hr/6min	900C/50min
9	CC	120	1.0E+16	850			5hr/40min	850C/2hr
10	CC	25	1.9E+17	700			7hr/49min	850C/2hr
	CC	120	3.0E+17	850			10 hours	400C/14hr
11	CC	25	5.0E+15	700			3hr/15min	
	CC	120	1.0E+17	800			4 hours	
12	CC	25	5.0E+16	700			1hr/32min	
	CC	120	1.4E+17	900			2 hours	
13	CC	120	3.0E+17	800	yes	H2	3hr/43min	
14	CC	120	3.0E+17	800	yes		3hr/28min	
15	CC	120	3.0E+17	800	yes	H2/CH4	4hr/26min	800C/1hr
16	CC	120	4.3E+17	900	yes	H2/CH4	6hr/12min	800C/1hr
17	CC	120	3.0E+17	700	yes	H2/CH4	5hr/10min	900C/90min
18	CC	120	2.3E+17	600	yes	H2/CH4	3hr/49min	
19	CC	120	3.0E+17	600	yes	H2/CH4	2hr/40min	900C/5hr
20	CC	120	3.0E+17	600	yes	H2/CH4	3hr/47min	950C/3hr
21	C	120	3.0E+17	600	yes	H2/CH4	4hr/4min	950C/2hr
22	CO	140	3.0E+17	850			3hr/17min	850C/1hr
23	CO	140	3.0E+17	700	yes	H2/CH4	2hr/31min	900C/3hr
24	CO	160	5.0E+17	750	yes	H2/CH4	4hr/53min	
25	CH4	140	2.4E+17	800			8hr/17min	
26	C	120	3.0E+17	700	yes	H2	3hr/40min	
27	C	25	3.0E+17	700	yes	H2	5 hours	
	C	120	3.0E+17	700	yes	H2	3hr/2min	
28	C	120	3.0E+17	750	yes	H2	3hr/7min	
29	C	120	5.0E+17	800	yes	H2	6hr/20min	
30	C	90	3.0E+17	700	yes	H2	3hr/49min	
	H2	25	1.6E+17	700	yes	H2	4hr/53min	
31	H2	40	1.1E+17	600			1hr/43min	
	C	120	3.0E+17	800	yes	H2	3 hours	
	H2	40	7.7E+16	800	yes	H2	1hr/28min	
32	C	120	3.0E+17	700	yes	H2	2hr/52min	
	H2	40	3.0E+17	850	yes	H2	3hr/20min	
33	H2	40	3.5E+17	600			3hr/48min	
	C	120	3.0E+17	800	yes	H2	2hr/56min	
34	H2	40	7.0E+16	750	yes	H2	3hr/2min	
35	C	120	3.0E+17	RT			3 hours	
	H2	40	3.0E+17	750	yes	H2	3hr/10min	
36	C	120	3.0E+17	RT			6hr/8min	
	H2	40	2.0E+17	850	yes	H2	3hr/33min	
37	C	120	3.0E+17	RT			4hr/14min	
	F	120	3.9E+17	850			3hr/5min	
38	C	120	3.0E+17	RT			5hr/17min	
	CC	120	8.8E+17	900	yes	H2	4hr/35min	
39	C	120	3.0E+17	RT			8hr/46min	
40	CC	120	3.0E+17	RT			3hr/17min	
	CC	120	4.5E+17	850			2hr/45min	
41	C	120	6.2E+16	850			10hr/3min	
42	C	120	2.3E+17	850			7hr/40min	
43	C	120	2.1E+17	900			27 hours	
44	C	120	3.0E+17	950			6 hours*	8 steps @3/4hr
							5hr/20min	

Table I  
Experimental Implant Conditions for Cu Substrate Tests



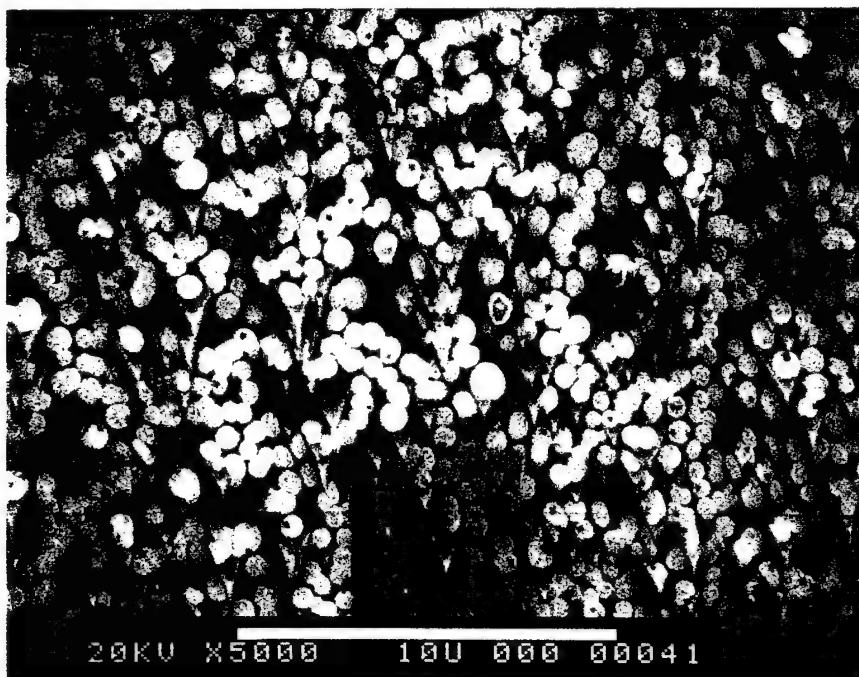
Many surface effects were observed in the various implantation-outdiffusion experiments. A number of effects were often observed on different areas of the same sample. These differences were usually related to orientations of individual crystals of the Cu substrate or to relative proximity to a hot filament source of atomic hydrogen background during the  $C^+$  implantation.

The effects of sublimation from the Cu surface were found to be of major importance. Low dose rate  $C^+$  implants performed at temperatures which involved significant sublimation provided some insight regarding development of the surface carbon layer. Figure 4 shows a view of a region of a Cu surface which was implanted at 850°C over a period of roughly 8 hours with 120 keV  $C^+$  ions to a dose of  $6 \times 10^{16} \text{ cm}^{-2}$ , a level almost an order of magnitude lower than the dose values usually employed. Implanted carbon appears on the surface in the form of discrete platelets. In another sample implanted at the same rate and temperature to a higher  $2.3 \times 10^{17} \text{ cm}^{-2}$  dose over 27 hours, the isolated platelets can be seen in Figure 5 to have merged into an almost continuous layer.

$C^+$  into Cu implants performed at temperatures below approximately 800°C did not result in carbon layers on the copper surface, but subsurface carbon layers were found to be produced. Figure 6 shows the result of using a dilute  $\text{HNO}_3$  etch to expose such a layer produced by  $C^+$  implantation at 700°C. Typically these subsurface layers appeared to be at least partially discontinuous.

At substrate temperatures of 800°C or higher during implantation, carbon was present on the surface upon completion of the implantation. Figure 7 shows a carbon surface layer typical of those produced by implantation at 800°C or higher. Figure 8 shows a more regular case produced using somewhat different conditions. These carbon network structures could be etch-released as films. Material of this type was originally described by Prins<sup>1</sup> and is believed to be mainly crystalline graphite with c-axis oriented perpendicular to the Cu surface<sup>6</sup>.

It is believed that during  $C^+$  implantation at high temperature, sublimation becomes nonuniform over the Cu surface as the density of implanted carbon near the surface increases. The presence of a carbon-rich layer appears to block sublimation from occurring over much of the Cu surface, but networks of fissures form in the surface layer and sublimation action then proceeds from the fissure channels which gradually increase in width and depth. The result is formation of a network of mesa-like surfaces covered by carbon and separated from each other by crevices which penetrate into the Cu. If a low temperature  $C^+$  implant is performed as an initial step prior to a high temperature  $C^+$  implant, the networks of surface crevices still form during the high temperature step. Figure 9 shows a typical example area.



Sample #41:

120 keV  $C^+$   
 $6.2 \times 10^{16} \text{ cm}^{-2}$   
 7 hrs/40 min  
 850°C

Figure 4  
 Carbon surface deposits after relatively  
 low dose, low rate  $C^+$  implant

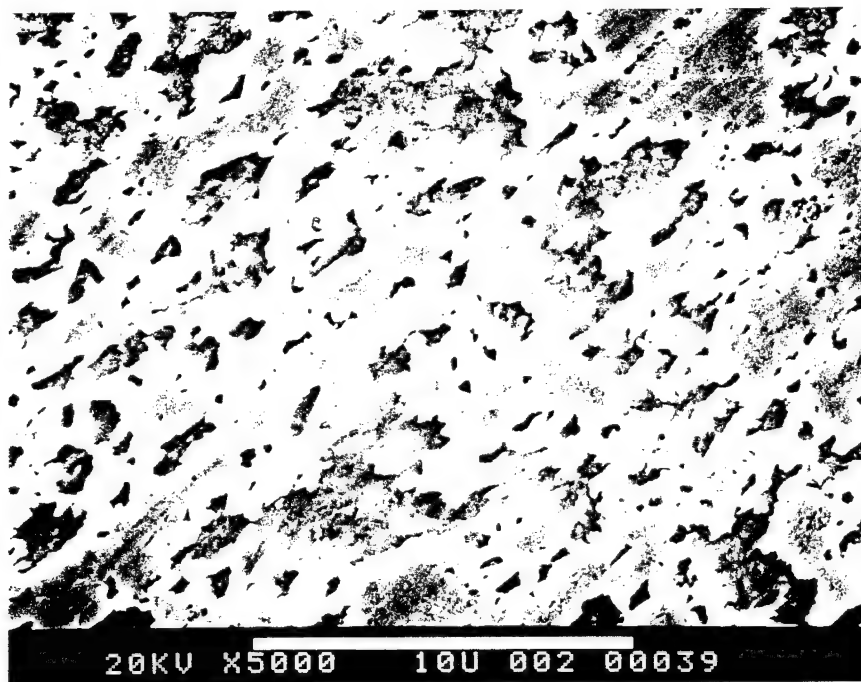


Sample #42:

120 keV  $C^+$   
 $2.3 \times 10^{17} \text{ cm}^{-2}$   
 27 hours  
 850°C

60° tilt

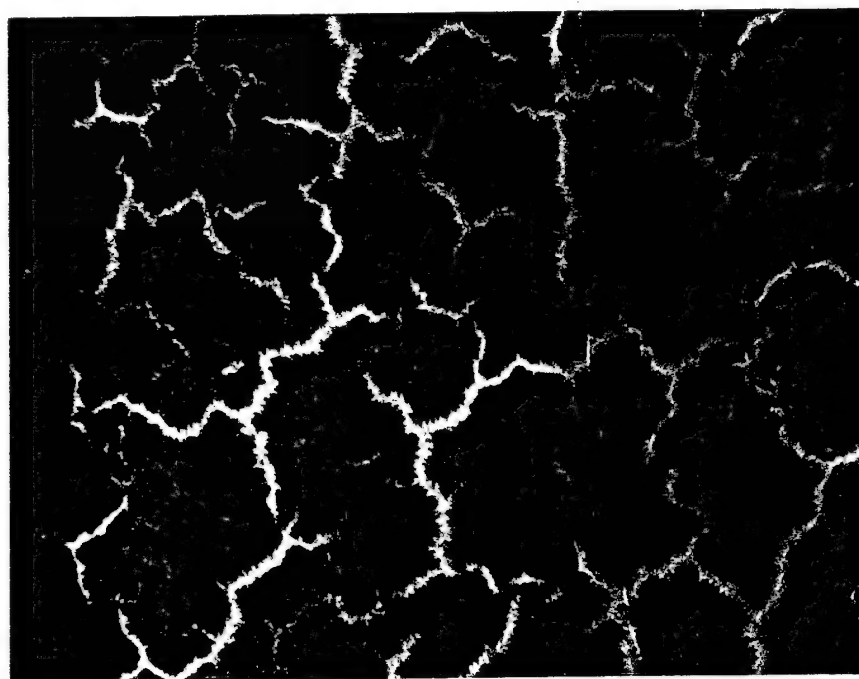
Figure 5  
 Carbon surface layer after long duration  
 low rate  $C^+$  implant



Sample #39:

120 keV C<sup>+</sup>  
 $3 \times 10^{17} \text{ cm}^{-2}$   
 Room Temp

Figure 6  
 Subsurface carbon layer exposed by etching



800x

Sample #12:

25 keV C<sup>+</sup>  
 $5.0 \times 10^{16} \text{ cm}^{-2}$   
 700°C

120 keV C<sup>+</sup>  
 $1.4 \times 10^{17} \text{ cm}^{-2}$   
 900°C

Figure 7  
 Optical micrograph of typical surface carbon layer  
 formed at temperature greater than 800°C

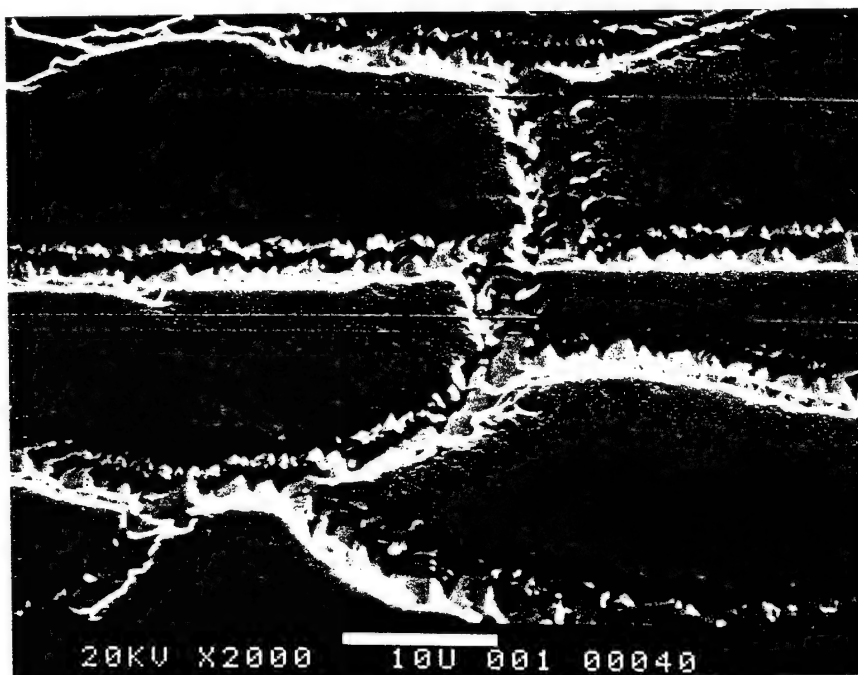


200x

Figure 8  
Optical micrograph of surface carbon layer  
formed at 800°C

Sample #13:

120 keV C<sup>+</sup>  
3.0 x 10<sup>17</sup> cm<sup>-2</sup>  
800°C



45° tilt

Figure 9  
Carbon-coated plateau areas  
separated by sublimation crevices

Sample #40:

120 keV C<sup>+</sup>  
3.0 x 10<sup>17</sup> cm<sup>-2</sup>  
Room Temp

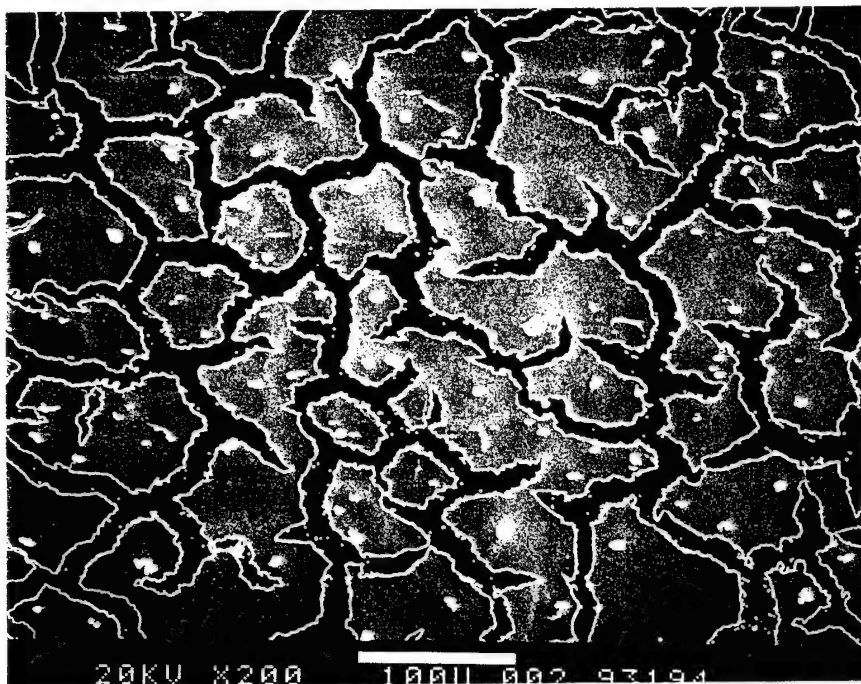
120 keV C<sup>+</sup>  
4.5 x 10<sup>17</sup> cm<sup>-2</sup>  
850°C

As crevice formation progresses due to Cu sublimation, C atoms present in an area being transformed into a crevice do not sublime. As part of the sublimation action, these carbon atoms are believed to accumulate along the crevice region walls, particularly near the rim. SEM examinations of crevice edges indicated that material believed to be carbon was usually present in the form of debris-like particles of no identifiable structure. CVD diamond growth onto such samples typically resulted in very dense, apparently random nucleation of diamond crystals within the mesa areas and almost no nucleation within the crevice areas. Figures 10 shows a representative SEM view.

Figures 11 and 12 are optical micrographs of structures typical of those formed on Cu surfaces by  $C^+$  implants at temperatures below  $800^\circ C$  followed by in-situ anneals at temperatures above  $800^\circ C$ . Although the oriented structures seen in these figures appear under the optical microscope to project above the Cu surface, SEM examinations show that these oriented structures consist of crater cavities with internal faces apparently aligned with the Cu grains. Figures 13 and 14 are typical examples. Micro-Raman examinations did not indicate the presence of diamond in the crater areas. During CVD growth onto such regions, diamond was found to nucleate preferentially around the crater openings and within the crater interiors as can be seen in Figure 15. The cavity structures aligned with the Cu host lattice are believed to form due to effects of sublimation at "blister" openings created in the carbon-rich Cu surfaces during high temperature heat treatment. The presence of implanted carbon close to the Cu surface strongly influences the way in which the Cu surface sublimates and in turn the manner of Cu sublimation defines the final condition of the implanted carbon.

Implantation of other ions before, during, or after introduction of  $C^+$  was found to alter the implantation-outdiffusion results. As one example, oxygen and carbon were implanted together as  $CO^+$  ions from carbon monoxide source gas.  $C^+$  and  $O^+$  in equal amounts into Cu at high temperature were found to leave the implanted surface with a fine matt texture having no evidence of residual carbon. The effect of the oxygen may have been due more to sputtering than to a chemical interaction. During CVD processing, no diamond nucleation was able to take place on the surfaces implanted by  $CO^+$ . Chemical etching of the Cu surface exposed some discontinuous buried carbon structure in the case of a sample implanted with  $CO^+$  at  $750^\circ C$ , but nothing observable in samples implanted at higher temperatures. Moderately high densities of diamond crystals were found to nucleate during CVD processing of all samples which had been implanted with  $CO^+$  and subsequently lightly etched to expose subsurface material.

Hydrogen was coimplanted with carbon by implanting  $CH_4^+$  ions from methane source gas. Implantation of  $2.3 \times 10^{17} CH_4^+$  ions/cm<sup>2</sup> at 140 keV and  $800^\circ C$  resulted in a surface carbon deposit and associated subsequent CVD diamond growth essentially identical to that produced by a similar dose of  $C^+$  alone at  $800^\circ C$ .



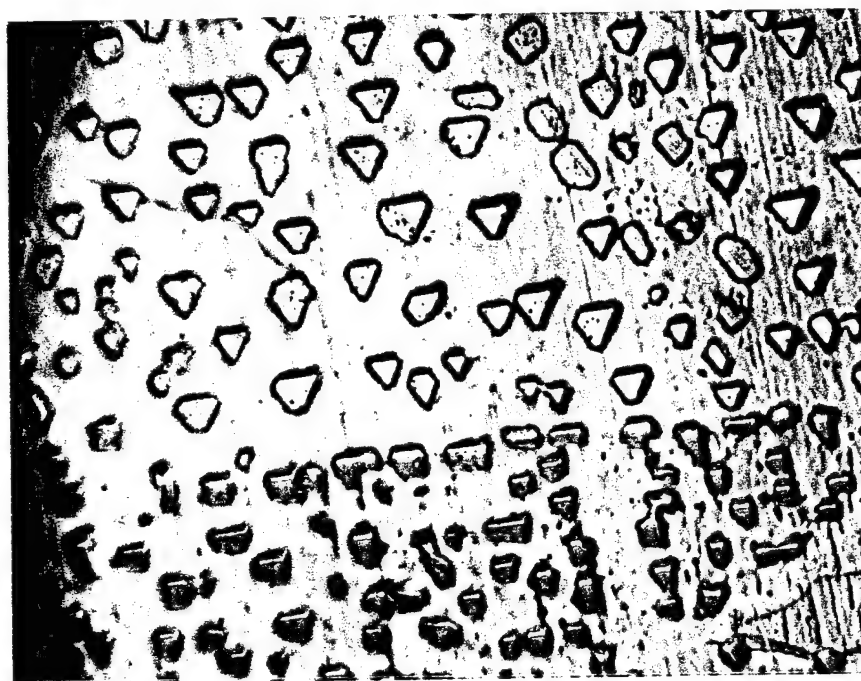
Sample #38:

120 keV C<sup>+</sup>  
 $3.0 \times 10^{17} \text{ cm}^{-2}$   
 Room Temp

120 keV C<sup>+</sup>  
 $8.8 \times 10^{17} \text{ cm}^{-2}$   
 900°C

Figure 10

Result of CVD onto surface with plateaus and crevices formed due to sublimation. Light areas are polycrystalline diamond



Sample #17:

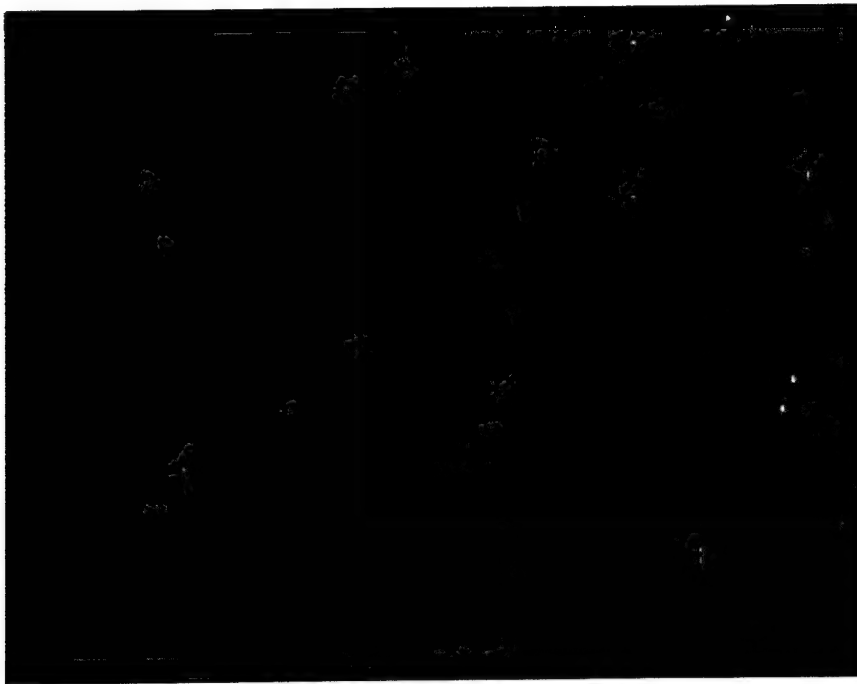
120 keV C<sup>+</sup>  
 $3.0 \times 10^{17} \text{ cm}^{-2}$   
 700°C

Anneal  
 90 min @ 900°C

800x

Figure 11

Optical micrograph of oriented structures formed by 700°C C<sup>+</sup> implant followed by 900°C anneal



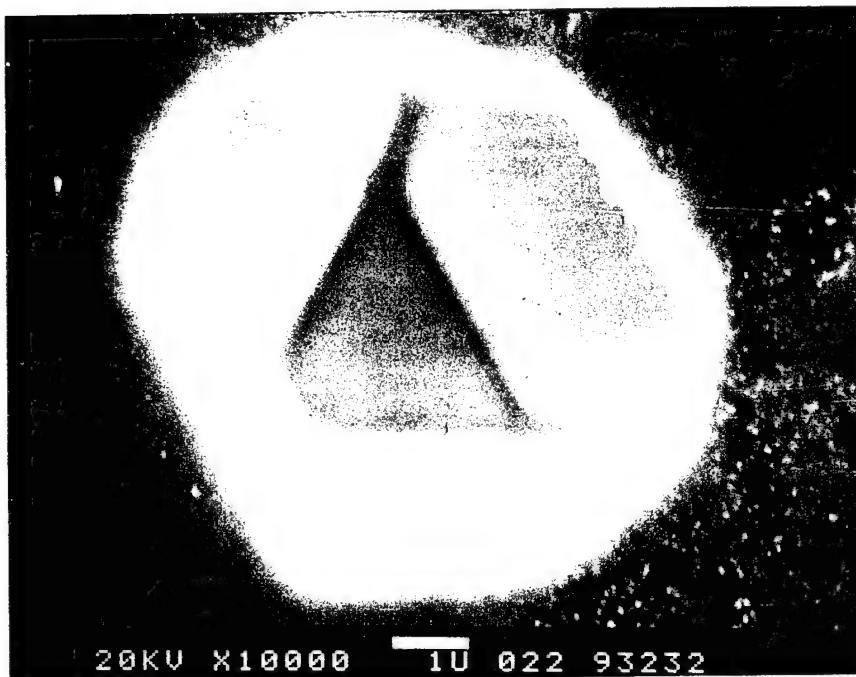
800x

Sample #17:

120 keV C<sup>+</sup>  
 $3.0 \times 10^{17} \text{ cm}^{-2}$   
 700°C

Anneal  
 90 min @ 900°C

Figure 12  
 Optical micrograph of oriented structures formed  
 by 700°C C<sup>+</sup> implant followed by 900°C anneal



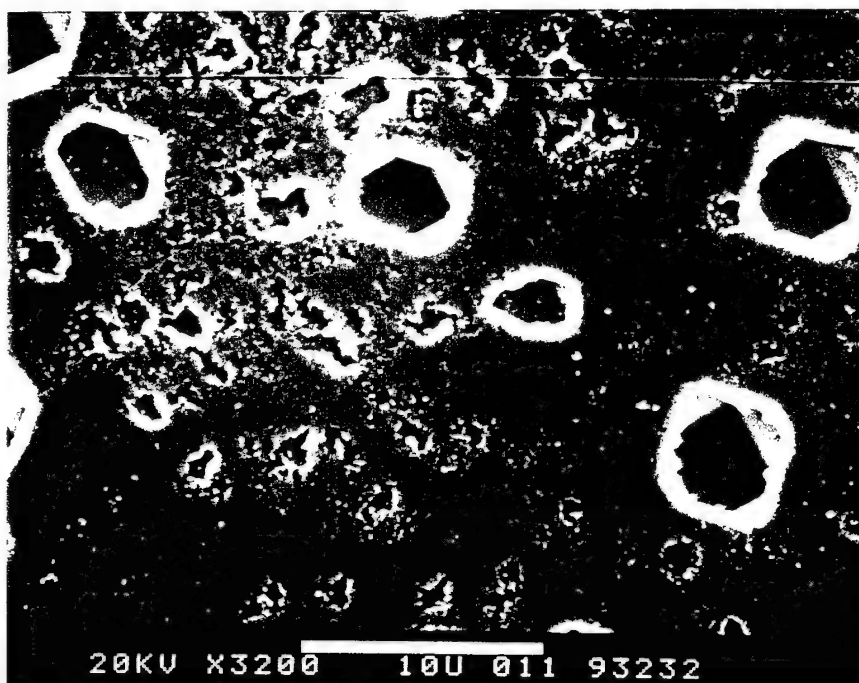
Sample #17:

120 keV C<sup>+</sup>  
 $3.0 \times 10^{17} \text{ cm}^{-2}$   
 700°C

Anneal  
 90 min @ 900°C

Figure 13  
 SEM view of oriented structure formed by 700°C C<sup>+</sup>  
 implant followed by 900°C anneal



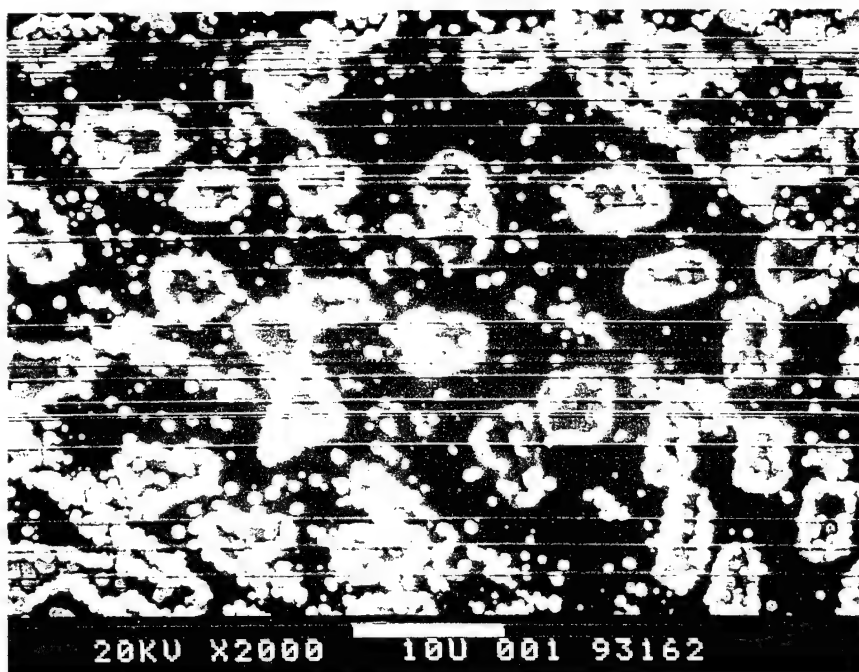


Sample #17:

120 keV C<sup>+</sup>  
 $3.0 \times 10^{17} \text{ cm}^{-2}$   
 700°C

Anneal  
 90 min @ 900°C

Figure 14  
 SEM view of oriented structures formed by 700°C C<sup>+</sup>  
 implant followed by 900°C anneal



Sample #17:

120 keV C<sup>+</sup>  
 $3.0 \times 10^{17} \text{ cm}^{-2}$   
 700°C

Anneal  
 90 min @ 900°C

Figure 15  
 CVD diamond formation on oriented crater field area



Results of implanting hydrogen before or after the  $C^+$  were found to be somewhat complex. For convenience,  $H_2^+$  ions produced from a hydrogen gas source were employed. During many of the experiments, a hot tungsten filament was present close to the substrate surface and  $10^{-3}$  torr of  $H_2$  was present as background gas during implantation. A particularly interesting result was obtained when an  $800^\circ C$   $C^+$  implant was followed by  $H_2^+$  also at  $800^\circ C$ . In the region of the sample surface which had been closest to the hot filament, the Cu appeared to be free of carbon after the implant. It is assumed that H bombardment consumed the carbon as rapidly as it appeared at the exposed surface. Further from the filament, a fractured crustlike layer formed upon the Cu. A fairly high density of local structures appeared which under the optical microscope look like oriented crystals. However, under the SEM these structures can be seen to be oriented cavities covered or partially covered by the crustlike coating. Figure 16 shows an example of an intact coating and the outline of a cavity below. During a diamond CVD process, densely nucleated polycrystalline diamond was found to grow upon the crustlike film.

When  $H_2^+$  was implanted at  $750^\circ C$  after a room temperature  $C^+$  implant, no carbon was found on the Cu surface. A relatively long etch in 2%  $HNO_3$  to remove surface copper exposed pieces of thin, brittle, uniform film material which was transparent under both the optical microscope and the SEM. Figures 17 and 18 show optical microscope and SEM views near the same edge of a piece of the material. The film appears smooth and featureless. All buried layers produced without hydrogen exhibited at least some degree of granularity, but the subsurface films formed by  $H_2^+$  implantation following the  $C^+$  exhibited no discernible structure.

One Cu sample was subjected to  $C^+$  and  $F^+$  implants. The effects of the fluorine were striking. Figures 19 through 21 show examples of regions of the Cu sample surface after  $3 \times 10^{17} \text{ cm}^{-2}$  120 keV  $C^+$  at room temperature followed by  $3.9 \times 10^{17} \text{ cm}^{-2}$  120 keV  $F^+$  at  $850^\circ C$ . No carbon was observable on the Cu surface after the  $F^+$  implant and only sparsely distributed diamond crystals resulted during CVD overgrowth. The fluorine caused anisotropic removal of material from the Cu surface as a result of chemical reaction and/or sputtering. This  $F^+$  result might represent a means to control the actions which take place as carbon locates itself on or within the copper. Alternatively, implantation of  $F^+$  at high temperature before the  $C^+$  might be useful in producing clean crystal faces upon the Cu in preparation for heteroepitaxy.

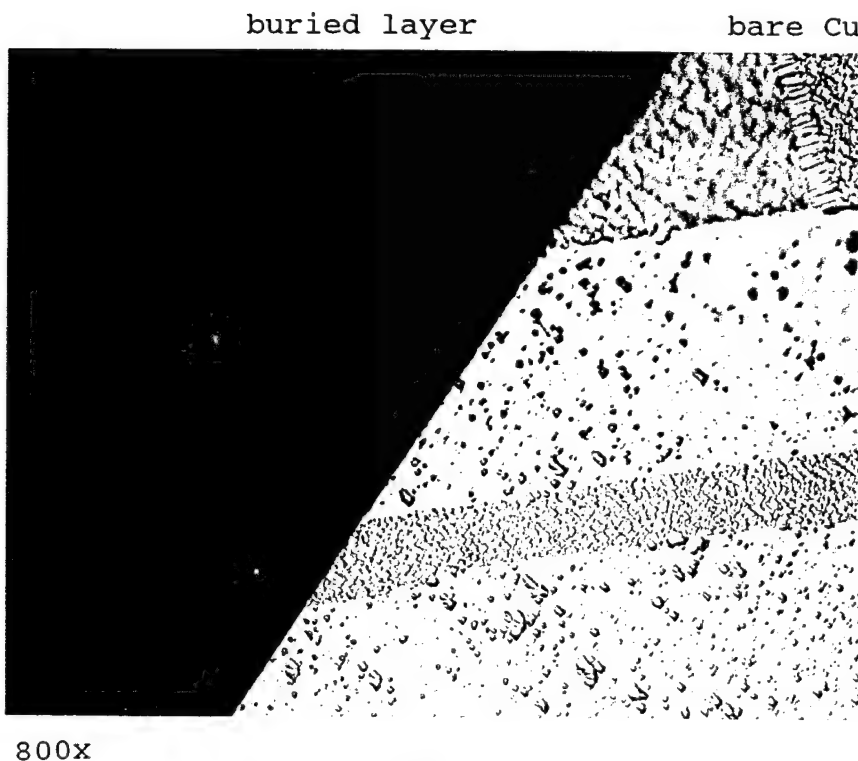


Sample #31:

40 keV  $C^+$   
 $1.1 \times 10^{17} \text{ cm}^{-2}$   
 600°C

120 keV  $C^+$   
 $3.0 \times 10^{17} \text{ cm}^{-2}$   
 800°C

Figure 16  
 Outline of oriented cavity covered by  
 coating after  $H_2^+$  and  $C^+$  implants

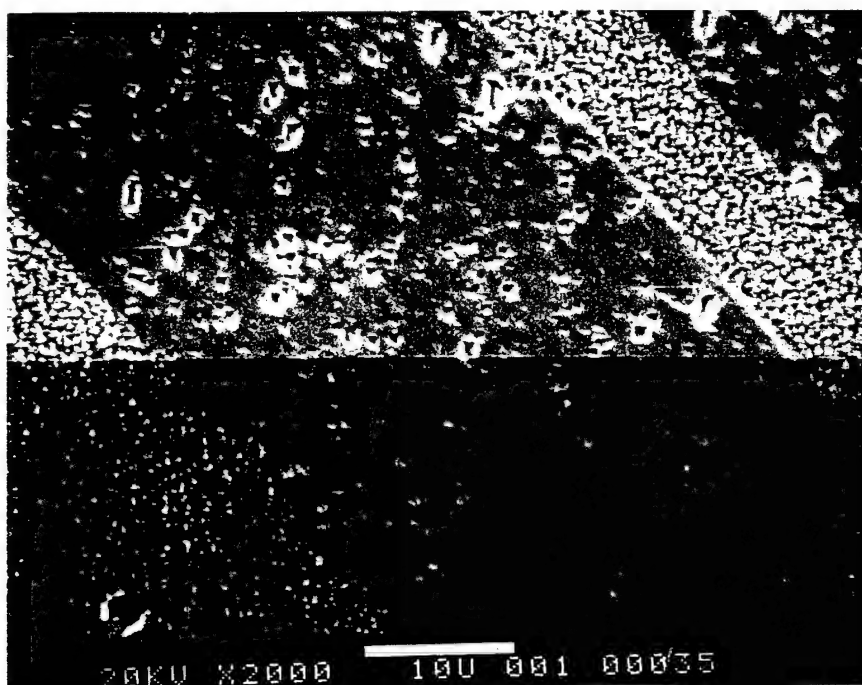


Sample #35:

120 keV  $C^+$   
 $3.0 \times 10^{17} \text{ cm}^{-2}$   
 Room Temp

40 keV  $H_2^+$   
 $3.0 \times 10^{17} \text{ cm}^{-2}$   
 750°C

Figure 17  
 Optical micrograph of  $C^+/H_2^+$  buried layer  
 material exposed by etching



bare  
Cu

buried  
layer

Sample #35:

120 keV  $C^+$   
 $3.0 \times 10^{17} \text{ cm}^{-2}$   
 Room Temp

40 keV  $H_2^+$   
 $3.0 \times 10^{17} \text{ cm}^{-2}$   
 750°C

Figure 18  
 SEM view of  $C^+/H_2^+$  buried layer  
 material exposed by etching



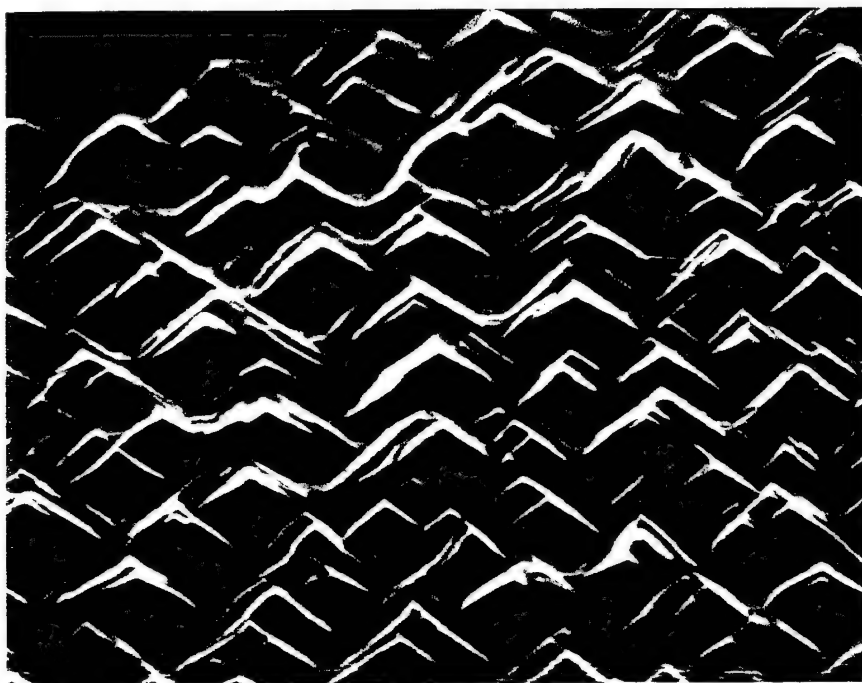
10,000X 60° tilt

Sample #37:

120 keV  $C^+$   
 $3.0 \times 10^{17} \text{ cm}^{-2}$   
 Room Temp

120 keV  $F^+$   
 $3.9 \times 10^{17} \text{ cm}^{-2}$   
 850°C

Figure 19  
 SEM view of surface structure formed by  
 $C^+$  implant followed by  $F^+$  Example #1



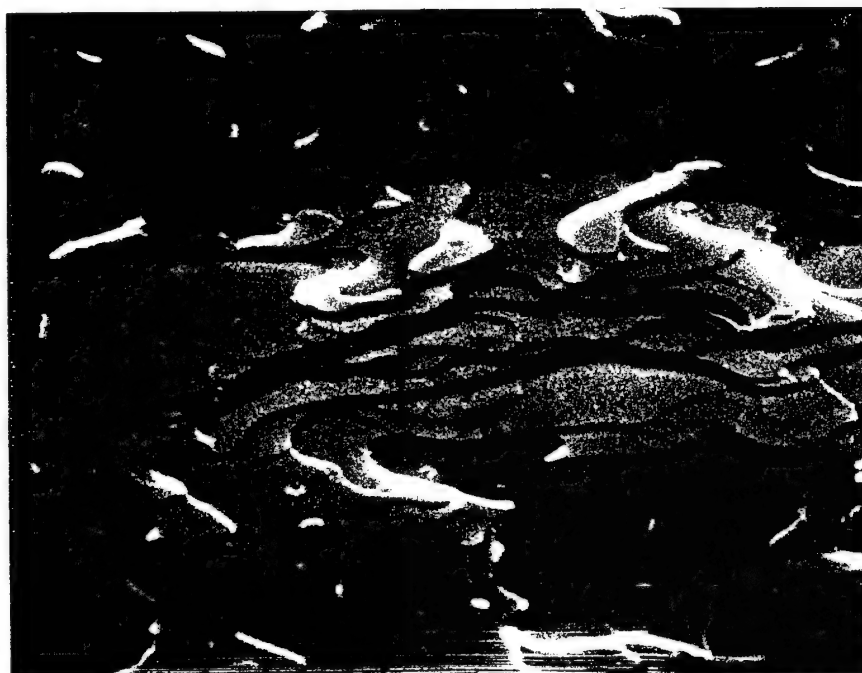
9,000X 60° tilt

Figure 20  
SEM view of surface structure formed by  
C<sup>+</sup> implant followed by F<sup>+</sup> Example #2

Sample #37:

120 keV C<sup>+</sup>  
3.0 x 10<sup>17</sup> cm<sup>-2</sup>  
Room Temp

120 keV F<sup>+</sup>  
3.9 x 10<sup>17</sup> cm<sup>-2</sup>  
850°C



10,000X 60° tilt

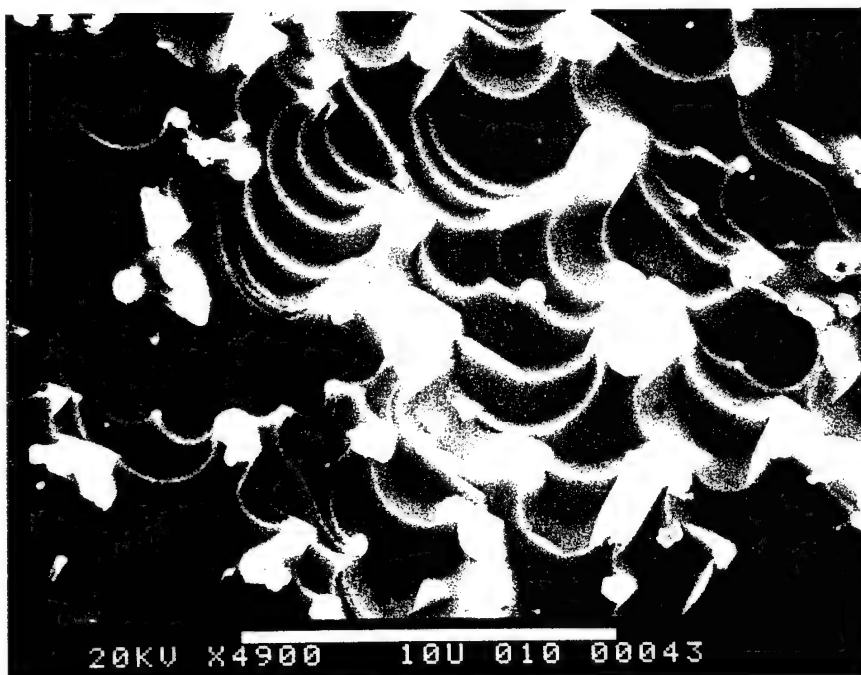
Figure 21  
SEM view of surface structure formed by  
C<sup>+</sup> implant followed by F<sup>+</sup> Example #3

Sample #37:

120 keV C<sup>+</sup>  
3.0 x 10<sup>17</sup> cm<sup>-2</sup>  
Room Temp

120 keV F<sup>+</sup>  
3.9 x 10<sup>17</sup> cm<sup>-2</sup>  
850°C

One Cu sample was implanted at 900°C by implanting 120 keV C<sup>+</sup> at moderate beam current for 15 minutes, annealing at 900°C in the absence of the beam for 30 minutes, implanting for 15 minutes, annealing for 30 minutes, and so on. A total of eight cycles was used to accumulate  $2.1 \times 10^{17} \text{ cm}^{-2}$  dose level. Figures 22 through 24 illustrate some of the surface structure which resulted. In these examples, the implanted carbon was believed to accumulated into isolated local deposits due to surface sublimation behavior. It is believed that sublimation action can become blocked at locations where sufficient carbon accumulates.

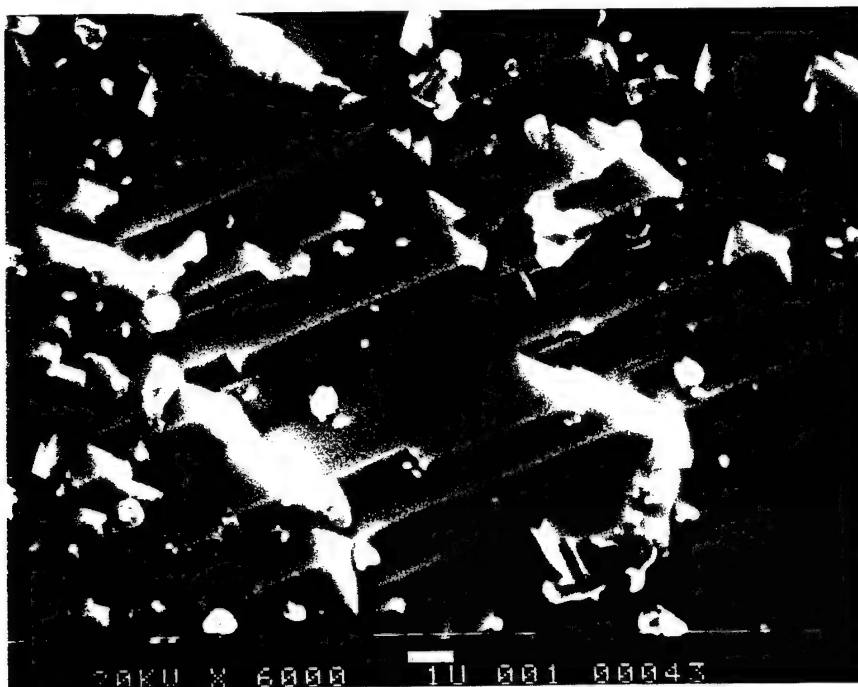


Sample #43:

120 keV C<sup>+</sup>  
 $2.1 \times 10^{17} \text{ cm}^{-2}$   
900°C

15 minute implants  
30 minute anneals  
8 cycles

Figure 22  
Surface structure formed by eight repetitions of  
15 minute C<sup>+</sup> implant/30 minute anneal at 900°C Example #1



Sample #43:

120 keV C<sup>+</sup>  
 $2.1 \times 10^{17} \text{ cm}^{-2}$   
 900°C

15 minute implants  
 30 minute anneals  
 8 cycles

Figure 23

Surface structure formed by eight repetitions of  
 15 minute C<sup>+</sup> implant/30 minute anneal at 900°C Example #2



Sample #43:

120 keV C<sup>+</sup>  
 $2.1 \times 10^{17} \text{ cm}^{-2}$   
 900°C

15 minute implants  
 30 minute anneals  
 8 cycles

Figure 24

Surface structure formed by eight repetitions of  
 15 minute C<sup>+</sup> implant/30 minute anneal at 900°C Example #3

The investigations described above demonstrated that, while a broad variety of surface modification effects could be produced on copper due to implantation of carbon ions and/or other ions, coordinated nucleation sites for diamond could not be formed.

The model for the concept of  $C^+$  into Cu implantation-outdiffusion heteroepitaxial diamond growth was based upon an assumption that, at sufficiently high temperatures, implanted carbon will diffuse through the crystal lattice of the copper host to reach the free surface. However, the experimental results suggested that it is invariably sublimation and not diffusion which determines the manner in which implanted carbon atoms actually arrive at the copper surface. Analytical calculations were made which confirm these observations.

Hertz-Knudsen theory of evaporation from a solid surface<sup>12</sup> predicts mass evaporation rate  $R$  from a surface consisting of atoms with mass  $m$  having vapor pressure  $p$  at temperature  $T$  as:

$$R = (m/2\pi kT)^{1/2} p$$

$$R = 5.8 \times 10^{-2} (M/T)^{1/2} p \quad g \text{ cm}^{-2} \text{ s}^{-1}$$

$M$  = molar weight  
 $p$  in torr  
 $T$  in °K

Using the expression above and handbook vapor pressure versus temperature data for copper<sup>13</sup>, expected rate of sublimation from a Cu surface as a function of temperature is as shown in Figure 25.

Predicted behavior shown in Figure 25 confirms that sublimation from a Cu surface undergoing implantation at high temperature will have large influence upon the resulting distribution of the implanted carbon. For example, experimental conditions which have been reported elsewhere to result in formation of single crystals of diamond on copper<sup>4</sup> were given as 900°C using an 8 hour  $C^+$  implant at 120 keV. Using the sublimation rate at 900°C from Figure 25, approximately 1.6  $\mu\text{m}$  of the Cu surface would be expected to be lost during implantation. The projected range of the 120 keV  $C^+$  ions in Cu is only about 0.16  $\mu\text{m}$ .

An experiment was conducted using 2 MeV He ion Rutherford backscattering apparatus at the University of Houston to monitor rates of accumulation of Cu deposited onto an aluminum foil due to sublimation from a hot Cu substrate located nearby. The experiment confirmed that the rate of sublimation from a Cu substrate at 900°C is sufficiently high that, during multiple hour  $C^+$  implants, the hot Cu surface does recede by much more than the range of the  $C^+$  ions.

Even a modest rate of sublimation of the copper host, leaving nonvolatile carbon behind to accumulate on the evolving surface, would have a substantial influence upon the dynamics of formation of a carbon layer in a  $C^+$  into Cu implantation-outdiffusion process. Rates of sublimation from Cu surfaces are actually so

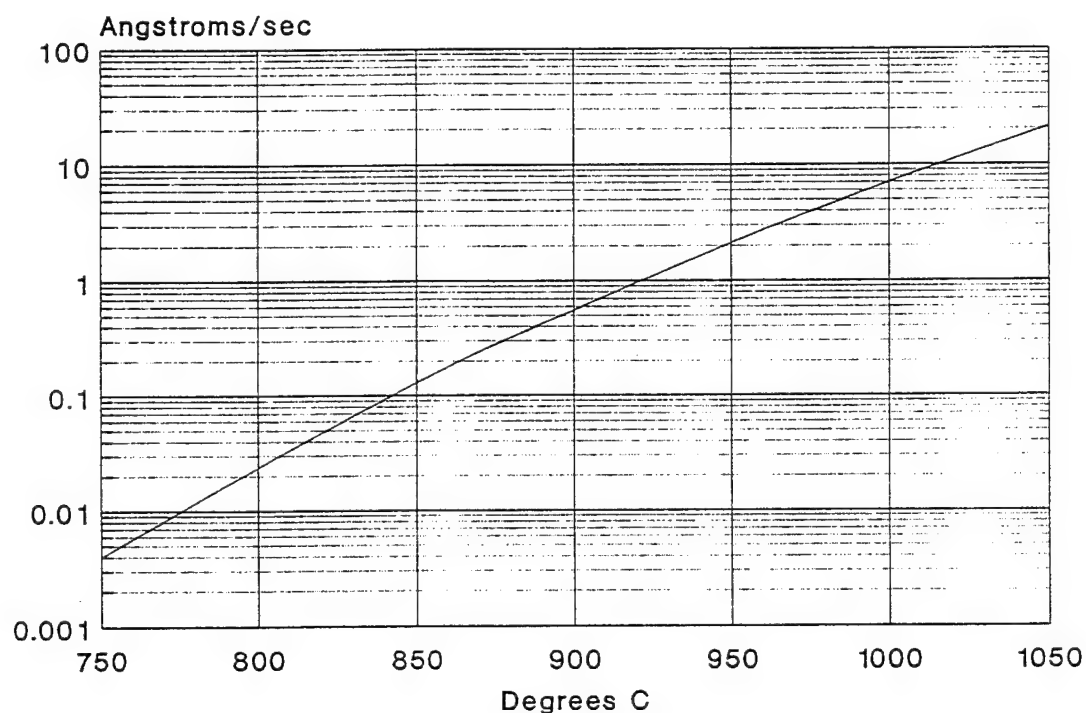


Figure 25  
Predicted Rate of Cu Surface Sublimation versus Temperature

high at temperatures above 800°C that sublimation is the dominant mechanism responsible for accumulation of carbon upon the surface of the copper substrate. The implanted carbon reaches the copper surface only because the copper surface recedes until the carbon becomes exposed. In spite of the otherwise attractive properties of copper, sublimation behavior effectively eliminates copper as a candidate to support heteroepitaxial growth of diamond by means of the implantation-outdiffusion concept.

### III.3 Investigations using Substrates other than Copper

Copper has been considered by most investigators to be the most suitable candidate substrate for heteroepitaxial diamond formation by an implantation-outdiffusion approach. From the investigations which were conducted under this program using copper substrates, it became evident that copper is not an acceptable substrate because the temperatures needed to promote diffusion of carbon within the copper are high enough to cause rapid sublimation of copper from the surface. A "template" for heteroepitaxial formation to be provided by the copper surface cannot exist because of the instability of that surface.



A substrate properly suited to support heteroepitaxial growth of diamond by an implantation-outdiffusion approach would be expected to exhibit a number of specific characteristics including:

- lattice constant similar to that of diamond
- absence of chemical interactions with carbon
- very low carbon solubility
- high melting temperature
- low vapor pressure at temperatures below 1000°C.

Other characteristics such as high diffusivity of carbon and absence of interactions with hydrogen would also be of importance. Unfortunately materials exhibiting all of these properties do not exist. Copper was generally considered to be the substrate of choice because it best satisfies the first four of the requirements above. Many materials meet some of the requirements. Several materials which meet some of the requirements, and a few which do not, were experimentally examined to determine whether they might be adaptable to produce conditions suitable for heteroepitaxial growth upon surface layers compositionally modified by high dose ion implantation. These included:

nickel  
niobium  
palladium  
molybdenum  
cobalt  
zirconium  
germanium  
silicon.

Investigations were conducted to try to utilize the specialized ion implantation capabilities established for copper in order to accomplish conditions for heteroepitaxy on these other materials. The investigations addressed the possibility that high dose ion implantation of hydrogen or carbon and hydrogen might be used to form surface layers of selected metal hydrides or metal-carbon-hydrogen ternary alloys upon which diamond growth might be favored over graphite formation in a suitable CVD process. Other researchers have shown that graphite formation can be suppressed on some hydride surfaces<sup>11</sup> and that oriented diamond growth can be produced upon a carbon-hydrogen ternary alloy layer formed on a nickel surface<sup>9,10</sup>.

High dose ion implantation can be used to radically alter the composition of a surface. It is feasible to employ implantation to create shallow tailored alloy layers upon surfaces of pure metal substrates. Hydride layers or carbon-hydrogen alloy layers might be formed by implantation on some metals such that these surfaces could become molten at temperatures far below the melting point of the metal element. Implanted hydrogen in these surfaces might be able to serve to suppress graphite formation in favor of diamond during CVD growth. Elemental substrates with such surfaces might

be able to support well-controlled oriented growth, a precursor for heteroepitaxy.

Table II lists some of the relevant characteristics of the materials which were investigated. Figure 26 shows vapor pressure versus temperature characteristics for these materials and Figures 27a through 27i show phase diagrams for their interactions with carbon.

	Crystal Structure	Lattice Constant Å	Melting Temperature °C	Vapor Pressure at 900°C Torr	C Solubility at 900°C Atomic %
Diamond	D-cubic	3.567			
Cu	f.c.-cubic	3.615	1085	$4 \times 10^{-6}$	0.02
Ni	f.c.-cubic	3.524	1455	$3 \times 10^{-9}$	0.9
Nb	b.c.-cubic	3.300	2477	negligible	forms a carbide
Pd	f.c.-cubic	3.890	1555	$4 \times 10^{-8}$	3
Co	hexagonal		1495	$4 \times 10^{-9}$	0.8
Zr	hexagonal		1855	negligible	forms a carbide
Si	D-cubic	5.431	1414	$3 \times 10^{-10}$	forms a carbide
Ge	D-cubic	5.657	938	$1 \times 10^{-7}$	negligible
Mo	b.c.-cubic	3.147	2623	negligible	forms a carbide

Table II  
Representative Characteristics of  
Candidate Substrate Materials

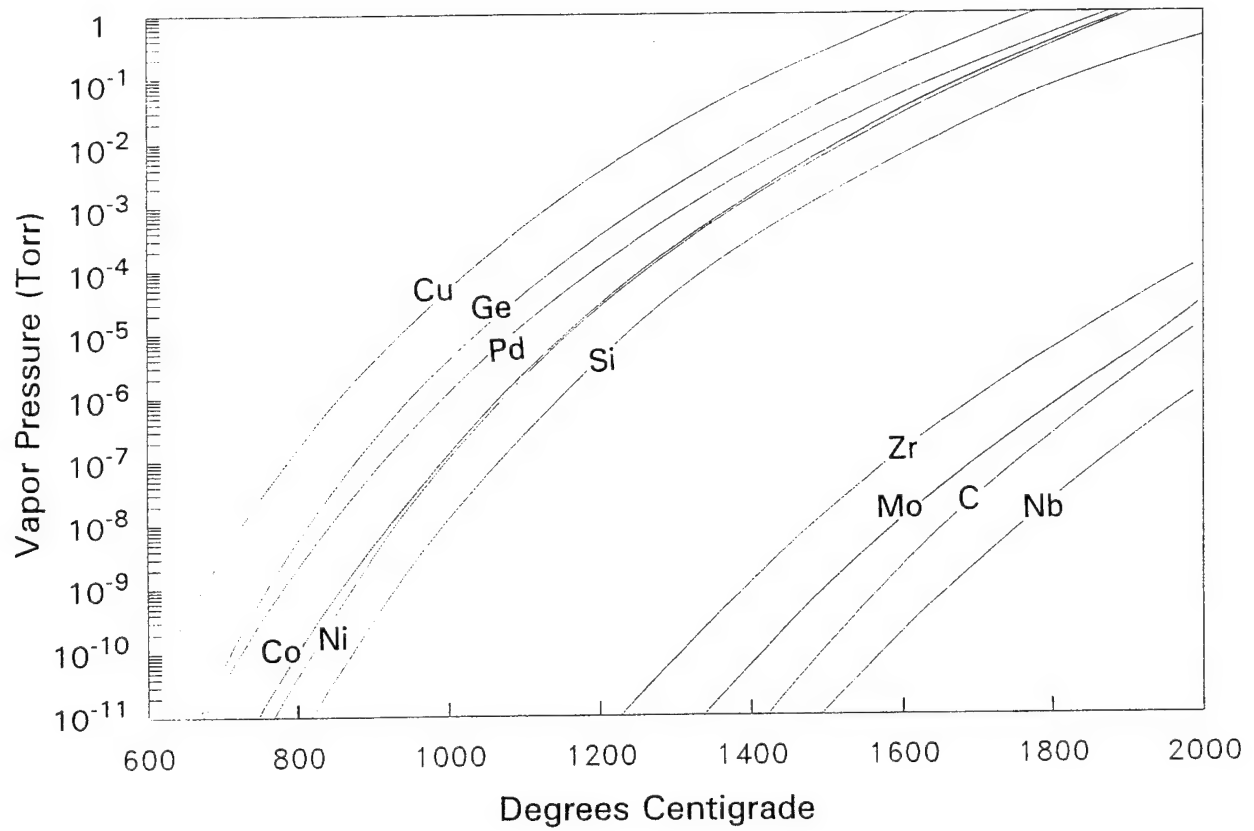
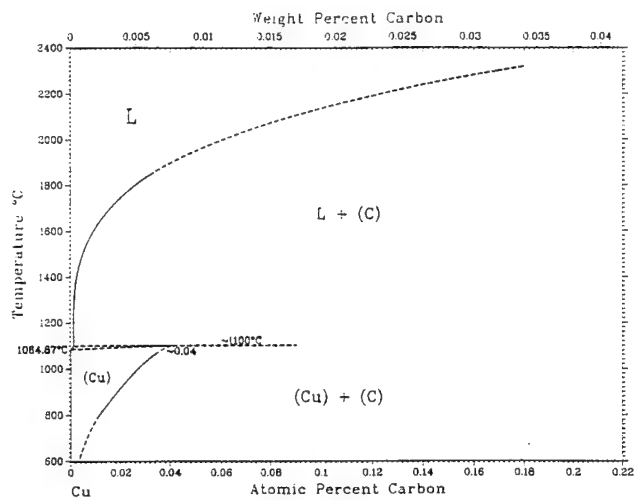
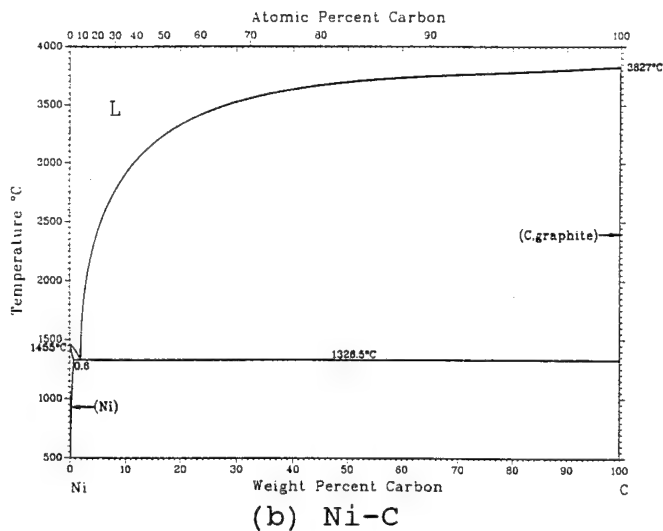


Figure 26  
Vapor pressure vs temperature characteristics  
of candidate substrate materials

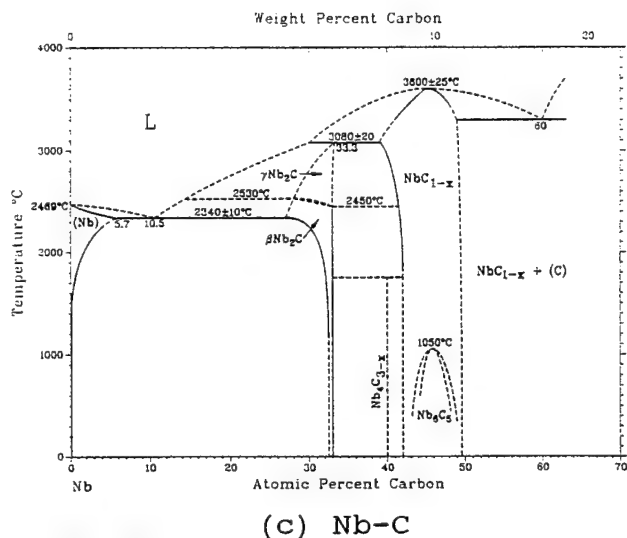
Cu-C Phase Diagram



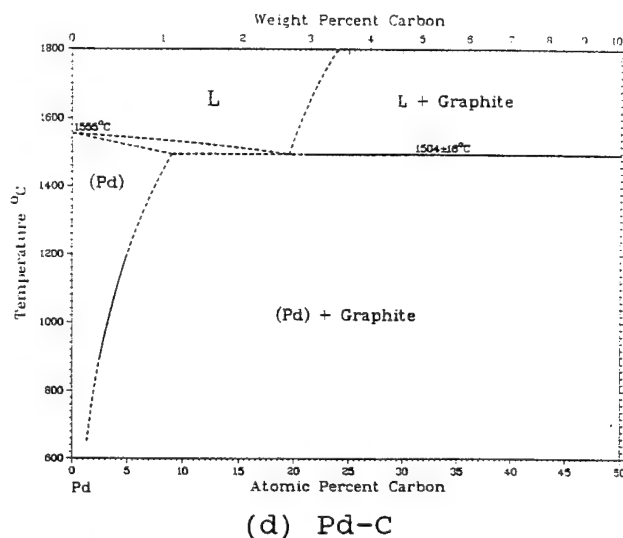
Ni-C (Graphite) Phase Diagram



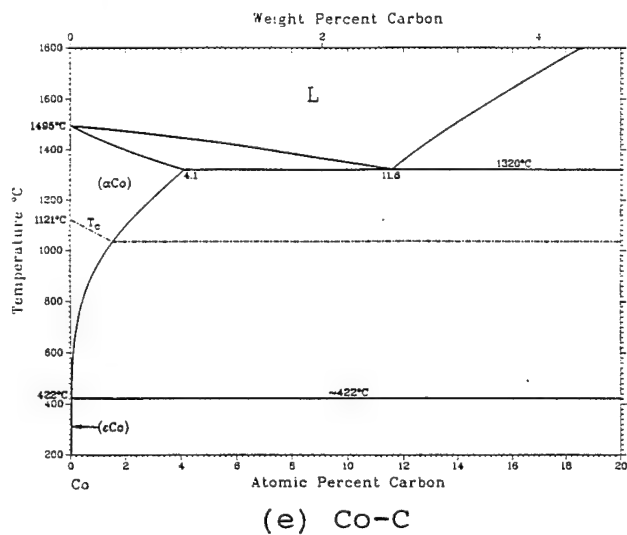
Nb-C Phase Diagram



Pd-C Phase Diagram



Co-C Phase Diagram



Zr-C Phase Diagram

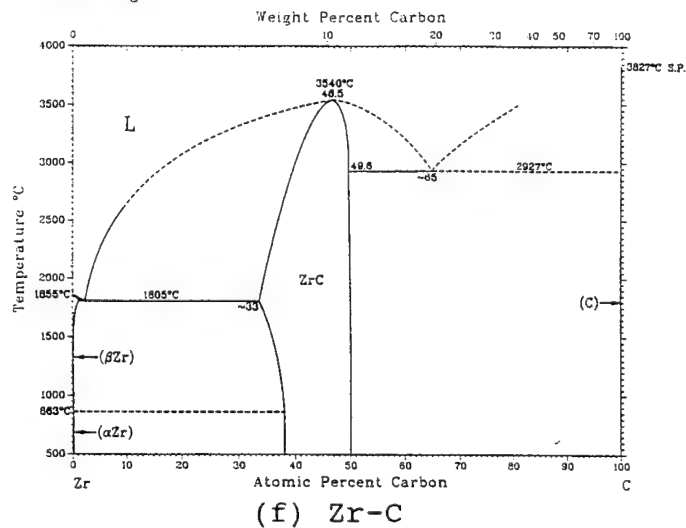
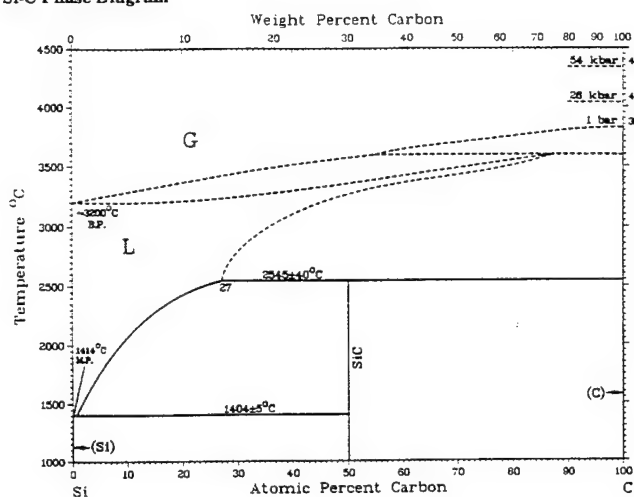


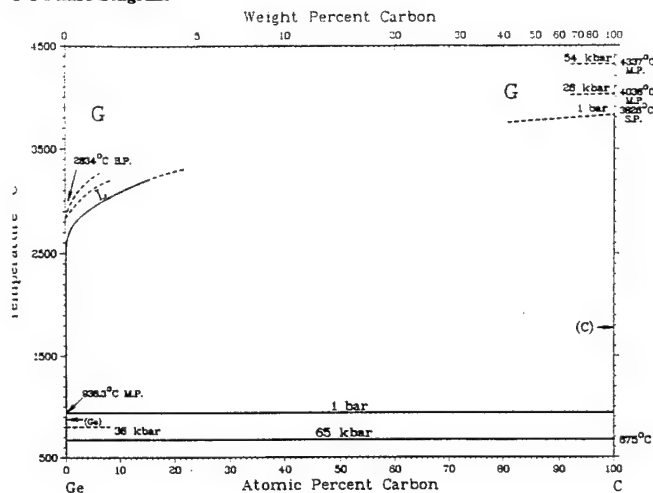
Figure 27 (a) - (f)  
Phase Diagrams of Candidate Substrates with Carbon

Si-C Phase Diagram



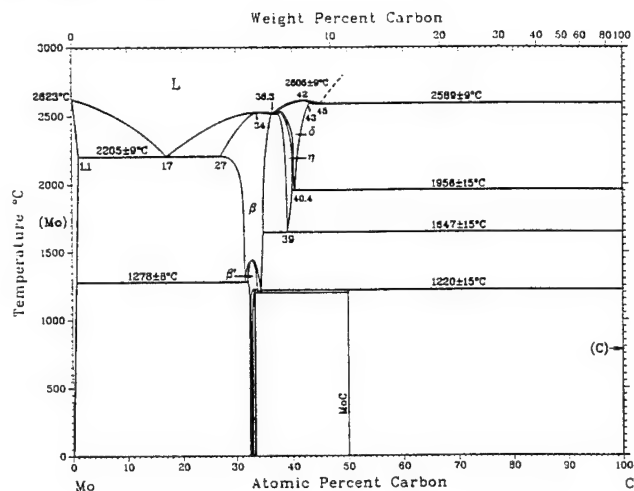
(g) Si-C

Ge-C Phase Diagram



(h) Ge-C

Mo-C Phase Diagram



(i) Mo-C

Figure 27 (g) - (i)  
Phase Diagrams of Candidate Substrates with Carbon

Several process variations were examined for each material including surface treatments or seeding operations performed prior to CVD diamond growth or as variations of the filament-assisted CVD growth process itself. The variations were somewhat different for each material, but they usually included most or all of the following:

- (1)  $C^+$  implantations into the growth surface
- (2)  $H_2^+$  implantations into the growth surface
- (3)  $C^+$  and  $H_2^+$  implantations into the growth surface
- (4) presaturation of substrates with carbon
- (5) diamond seeding
- (6) high temperature treatments immediately before CVD growth.

High dose  $C^+$  implantations were employed to assess compatibility of the subject substrates with the basic implantation-outdiffusion approach. High dose  $H_2^+$  implantations were utilized to produce hydrogen rich alloy surfaces which might be capable of suppressing graphite formation during initial stages of diamond growth. Combined  $C^+$  and  $H_2^+$  implants were used with the intention of trying to form low melting point shallow surface layers capable of supporting oriented seeding techniques<sup>9,10</sup>.

As can be noted in the phase diagrams which were shown in Figure 27, solubility of carbon is small, but not negligible, at high temperatures in several of the materials which were examined. During high temperature processing, these materials typically consume surface carbon--ion implanted carbon, carbon from diamond seeds, and also available carbon from vapor reactants of a CVD diamond growth process. In order to try to minimize these carbon dissolution effects, some substrates were subjected to preliminary treatments intended to produce carbon saturation in the vicinity of their surfaces. Carbon surface sources were applied by evaporation or by application of colloidal carbon and the substrates were then subjected to long duration high temperature furnace treatments.

Diamond seeding operations were performed (1) by ultrasonic agitation in an alcohol bath containing small diamond particles, and (2) by depositing diamond powder in alcohol mixture directly on the surface and allowing the alcohol to dry. The ultrasonic seeding procedure is usually able to produce high nucleation densities, but leaves almost no detectable diamond mass resident upon the surfaces. The seeding action is believed to be due to submicroscopic fragments of the diamond particles which become embedded in the surface during ultrasonic bombardment. The direct deposition method leaves relatively high densities of diamond particle seeds upon the surface.

Pre-growth high temperature treatments were performed for the purpose of establishing conditions which might allow seed particles to orient themselves relative to the lattice of the substrate<sup>9,10</sup>. Temperatures up to several hundred degrees higher than the normal temperature of approximately 950°C used for filament-assisted CVD diamond growth were used for brief periods ranging from a few

seconds to several minutes. It was anticipated that shallow surface alloy layers created by ion implantation of high concentrations of carbon and hydrogen might be caused to melt during these temperature excursions so as to allow seed particles to reorient themselves with respect to the underlying lattice during subsequent resolidification.

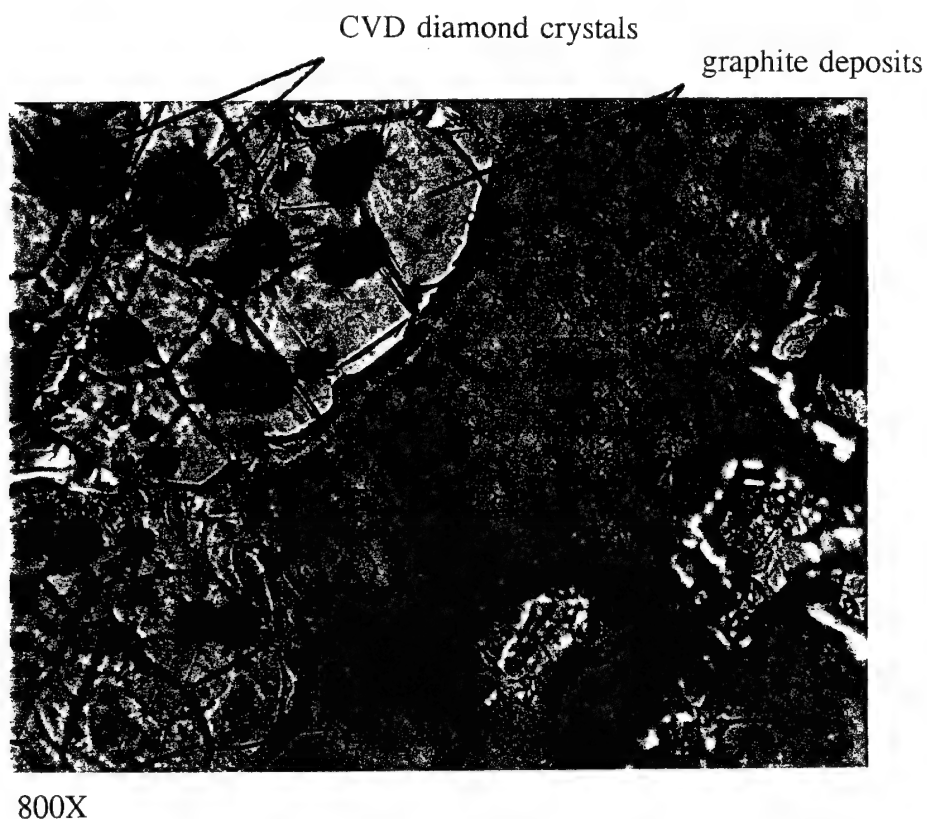
Nickel was used as the substrate material for a large number of tests involving broad variations of implantation parameters, carbon saturation, diamond seeding procedures and thermal pre-treatment parameters. Nickel has a lattice parameter very close to that of diamond, does not react with carbon at temperatures below about 1500°C, and has a vapor pressure more than three orders of magnitude lower than that of copper at 1000°C. At high temperatures, nickel is an effective solvent for substantial amounts of carbon. The formation of films of oriented graphite upon nickel foils containing dissolved carbon has been a subject of research interest for several decades<sup>16,17,18</sup>.

At temperatures needed for CVD diamond growth, the solid solubility of carbon in nickel is quite high and carbon from any source will readily dissolve. Carbon introduced into nickel surfaces by ion implantation was found to be rapidly dissipated from the implanted surface regions as a result of high temperatures during implantation and/or during subsequent CVD processing. Similarly, most diamond seeds were found to dissolve and to be eliminated as nucleation sites during the initial stages of CVD growth. As a result, nucleation densities resulting on Ni during CVD growth were observed to be lower than those produced by identical seeding processes on some other materials such as silicon.

Upon cooling after any high temperature procedure, graphite surface layers and sometimes fractured thicker graphite deposits were found to form upon Ni substrates into which carbon had been introduced by ion implantation or by dissolution of diamond seed particles. Figure 28 shows a typical surface micrograph.

Under SEM examinations, the nucleation sites for CVD diamond grown on carbon-implanted nickel substrates were found primarily at cracks or discontinuities in graphite films which were always present. The effect was apparently identical to that observed in the case of diamond growth on carbon-implanted copper substrates, ie., nucleation takes place preferentially on the prism planes of the graphite<sup>6</sup>.

None of the process variations employed, or combinations of them, produced any substantially different result. Implanted hydrogen was not effective in eliminating formation of graphitic layers or in altering the diamond nucleation behavior. Presaturation of the nickel substrates with carbon introduced by high temperature diffusion resulted in more dense graphitic layers and reduced diamond nucleation densities. Temperature excursions to between 1050°C and 1300°C performed in-situ immediately prior to initiation of filament-assisted CVD growth also resulted in lower nucleation



Implanted:

30 keV  $H_2^+$   
 $1.0 \times 10^{17} \text{ cm}^{-2}$   
 Room Temp

30 keV  $C^+$   
 $9.0 \times 10^{17} \text{ cm}^{-2}$   
 Room Temp

Figure 28  
 Optical micrograph of formations on implanted  
 Ni surface following filament-assisted CVD

densities unless the duration of the excursion was limited to a few seconds. None of the diamond growth produced on nickel exhibited evidence of orientation relative to the substrate crystal structure.

The experimental variations utilized for nickel were also evaluated on several other selected substrate materials: niobium, palladium, cobalt, molybdenum, and zirconium. In the cases of Nb, Pd and Co, the results were essentially similar to those on Ni. Implanted carbon and diamond seeds could be readily dissolved into these substrates at high temperatures and, upon subsequent cooling, thin surface layers believed to be graphitic carbon would form. These actions tended to result in suppression of diamond nucleation during filament-assisted CVD and low densities of diamond crystals would form, primarily upon the graphite layer edges and cracks.

Diamond nucleated densely and grew well on seeded molybdenum and on zirconium, particularly so on zirconium. Implanted  $C^+$ , or  $C^+$  and  $H_2^+$ , did not nucleate diamond growth on these metals in the absence of a seeding operation. Zirconium itself became badly embrittled by diamond CVD processing, but it is suspected that thin interfacial layers of deposited or implanted zirconium might contribute to effective diamond growth on other substrates.



Germanium does not have properties which would allow it to be considered as candidate implantation-outdiffusion substrate. It has a lattice parameter very dissimilar to that of diamond, it has a much higher coefficient of thermal expansion than diamond, and it has high vapor pressure at the temperatures normally used for diamond growth. It was included in the experimental study in order to observe the growth behavior of diamond on a molten surface. Substrate temperatures in the standard filament-assisted CVD diamond growth process used during this work were typically between 950°C and 1000°C. The melting temperature of germanium is 937°C and, during CVD growth, germanium samples melted. Diamond was observed to nucleate easily and grow readily upon molten germanium, even in the absence of seeding or carbon implantation. Due to the expansion coefficient mismatch, diamond coatings delaminated from the germanium during cooling. Under the conditions utilized, the diamond coatings formed on germanium were polycrystalline and showed no preferential orientation.

Silicon is not a material which could be used for a carbon outdiffusion process. When carbon is implanted to high dose into silicon at high temperatures, the carbon reacts to form silicon carbide and it is believed that single crystal  $\beta$ -SiC can be produced<sup>19,20</sup>. Single crystal SiC is one of the few materials upon which oriented diamond growth has been accomplished<sup>21,22</sup>. Silicon was included in the present investigation to determine whether a SiC layer formed by high temperature reactive ion implantation might be suitable as an oriented growth interface. The silicon samples were the last materials investigated during the program.

Several single crystal silicon disk samples were subjected to high dose  $C^+$  implants at 975°C. Infrared transmittance measurements indicated the formation of SiC by a characteristic transmittance dip centered at  $800\text{ cm}^{-1}$  ( $12.5\mu\text{m}$ ). Figure 29 is an FTIR spectrum which shows the transmittance of an implanted sample relative to that of an identical unimplanted silicon disk. Silicon disks implanted with  $C^+$  at high temperatures were subjected to filament-assisted CVD using an initial bias-enhanced nucleation procedure<sup>23</sup>. Microscopic examinations made after only a few hours of CVD growth showed the early stages of growth to be characterized by a considerable degree of common orientation of the individual diamond crystals, but also by substantial contents of randomly oriented crystals among the high density of growth sites. It is believed that the densities of nonoriented growth sites would be reduced or possibly eliminated by improvement of the bias-enhanced nucleation technique.

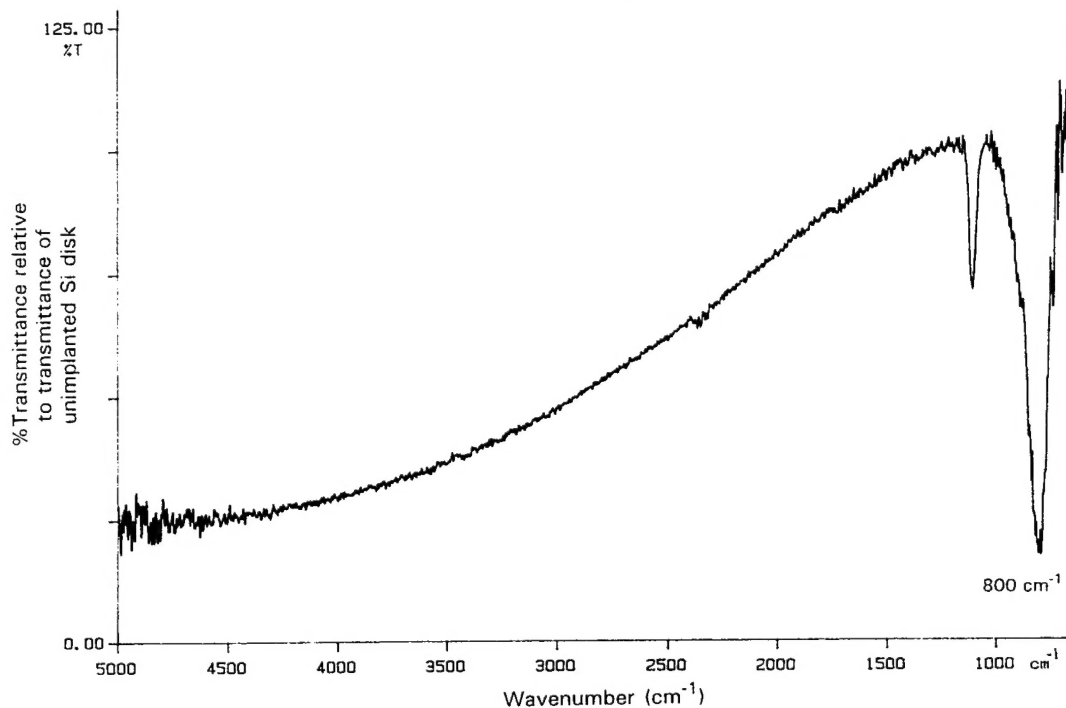


Figure 29  
FTIR spectrum from Si disk implanted at 975°C  
with 45 keV C<sup>+</sup> to  $1 \times 10^{18}$  ions/cm<sup>2</sup>

#### IV. SUMMARY

This investigation has not been successful in establishing an implantation-outdiffusion approach able to produce heteroepitaxial nucleation of diamond on a nondiamond substrate. The investigation has included a number of host substrate materials, a considerable range of conditions for ion implantation of carbon, and a substantial number of variations of auxiliary procedures intended to suppress graphitic carbon formation. Over this range, there has been no evidence of the formation of diamond rather than graphite due to outdiffusion of implanted carbon from an implanted substrate. These observations are consistent with reported results from previous investigations of the migration of carbon at high temperatures within a number of metals. Thermodynamic fundamentals appear to have favored formation of nondiamond phases of carbon rather than diamond under all observed conditions which allowed implanted carbon to migrate to the surfaces of host substrates.

Even if diamond were to be favored as the form to be taken by implanted carbon caused to migrate at high temperatures to a host substrate surface, the properties to be required of the substrate might not be possible to satisfy by any existing materials. The

implantation-outdiffusion approach is based upon the assumption that implanted carbon will not be soluble in or chemically reactive with the substrate and, at sufficiently high temperature, will be free to migrate to the substrate surface. Materials with these properties, and with a crystal structure somewhat similar to that of diamond, may not exist.

Copper has been considered the most plausible candidate to support heteroepitaxy of diamond by means of carbon implantation-outdiffusion. Carbon is almost insoluble in and unreactive with copper, even at high temperatures, and copper does have a potentially compatible crystal structure for diamond. However, the investigations of this program have shown that ion implanted carbon will not diffuse to a copper surface at temperatures below levels at which the copper undergoes rapid sublimation. Implanted carbon atoms actually reach a copper surface only because sublimation causes the surface to recede to expose the carbon. Under these circumstances, a mechanism for heteroepitaxial layer formation is not available.

Other materials which offer better thermal stability than copper, such as nickel, involve incompatibilities with other implantation-outdiffusion requirements. Typically, their carbon solubility characteristics at high temperatures are too high. Implantation is a surface treatment process: even at very high ion doses, the total amount of implanted mass is always extremely small. Implantation cannot be used to introduce sufficient carbon into any material in which carbon solubility is not negligible. Efforts to presaturate various substrate materials with carbon introduced by diffusion at high temperatures did not significantly alter the diamond nucleation behaviors observed on these materials.

Investigations were made to try to employ ion implantation of hydrogen or hydrogen and carbon together to form surface alloys upon which graphite formation at high temperatures would be suppressed. These approaches were typically not productive for the same reasons that implantation of carbon into materials in which carbon is soluble were not effective. At high temperatures, either during implantation or during CVD diamond growth, the implanted constituents invariably dissolved within the host and migrated from the vicinity of the implant surface.

Some high temperature implantation variations might offer promise for orientated diamond growth by reactive formation of intermediary layers rather than by implantation-outdiffusion. Ion implanted carbon can react at high temperatures with some substrates to form heteroepitaxial carbide layers which might eventually be adapted to serve to support heteroepitaxial diamond growth. Silicon implanted with carbon at high temperatures to form a crystalline silicon carbide layer was found to be one promising example.

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